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<b>(21) International Application Number:</b> PCT/GB98/00757 <b>(22) International Filing Date:</b> 13 March 1998 (13.03.98)  <b>(30) Priority Data:</b> 9705187.4 13 March 1997 (13.03.97) GB  <b>(71) Applicant (for all designated States except US):</b> UNITED DISTILLERS PLC [GB/GB]; Distillers House, 33 Ellersly Road, Edinburgh EH12 6JW (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CAMERON, Allan [GB/GB]; 33 Llythrid Avenue, Uplands, Swansea SA2 0JJ (GB). GEORGE, Simon [GB/GB]; 28 Bethania Road, Clydach, Swansea SA6 5DE (GB). LEDGER, Richard [GB/GB]; 1 Pyle Road, Bishopston, Swansea SA3 3HH (GB). JONES, Gary [GB/GB]; 13 Neath Road, Resolven, Neath, West Glamorgan SA11 4AA (GB).  <b>(74) Agent:</b> BOULT WADE TENNANT; 27 Fumival Street, London EC4A 1PQ (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> With international search report.
<b>(54) Title:</b> METHOD OF MARKING GLASSY THERMOPLASTIC POLYMERIC MATERIALS  <b>(57) Abstract</b>  There is described a method of providing a glassy thermoplastic polymeric material having a glass transition temperature in excess of 80 °C with a sub-surface mark. The method comprises the steps of directing at a surface of the glassy thermoplastic polymeric material a beam of laser radiation to which the glassy thermoplastic polymeric material is substantially opaque. The beam energy absorbed at the surface of the glassy thermoplastic polymeric material is sufficient to produce localised stresses within the glassy thermoplastic polymeric material at a location spaced from the surface without any detectable change at said surface. The localised stresses thus produced are normally invisible to the naked eye but are capable of being rendered visible under polarised light. There is also described a body of glassy thermoplastic polymeric material comprising a mark obtained in accordance with the above method.		

## Description

### METHOD OF MARKING GLASSY THERMOPLASTIC POLYMERIC MATERIALS

The present invention relates to a method of providing a body of glassy thermoplastic polymeric material with a sub-surface mark that is invisible to the naked eye but which is capable of being rendered visible under polarized light.

Many products are made of glassy thermoplastic polymers such as polycarbonate, polymethylmethacrylate, polystyrene and polyvinyl chloride and there has been a desire for many years to provide a method of marking products of this type so that once a mark has been applied, it cannot be removed. Clearly such a method of marking would have a wide range of applications, not least in combatting parallel trading.

In the past, in order to produce an indelible mark, manufacturers have relied, almost exclusively, on surface marking. However, the problem with this type of mark is that it may either be destroyed by removing that part of the surface on which the mark is applied, or imitated by the application of an identical mark on a substitute container.

In order to overcome these problems, the Applicant developed a method and apparatus for providing a body of material with a sub-surface mark which are described in International Patent Publication No. WO 92/03297. The method described comprises the steps of directing, at a surface of the body, a high energy density beam to which the material is transparent and bringing the beam to a focus at a location spaced from the surface and within the body so as to cause localised ionization of the material and the creation of a mark in the form of an area of increased opacity to electromagnetic radiation substantially without any detectable change at the surface. This provided the advantage that the resulting mark was both difficult to imitate and near impossible to remove.

In order to provide a method of marking having further advantages, it can be desirable that the resulting mark is invisible to the naked eye. In this way, a potential counterfeiter will not only have difficulty in removing or imitating the mark, but will also run into problems in locating the mark in the first place.

U.S. Patent No. 3,657,085 describes a method of providing a transparent material, such as glass, with a sub-surface mark using an electron beam but also mentions the possibility of using a laser beam as an alternative. The object of the U.S. patent is to provide a method of marking an article, such as a spectacle lens, with an identification mark which is normally invisible but which can be rendered visible when required.

To this end, the electron, or laser beam, is directed onto a mask placed over the spectacle lens so that that part of the beam passing through the cut-out portions of the mask, impinges upon the material of the spectacle lens. The beam is scattered by collisions with the molecules of the material that makes up the lens with the result that the kinetic energy of the beam is absorbed as heat producing permanent stress patterns within the lens. These stress patterns are invisible to the naked eye but may be rendered visible by double refraction in polarized light.

When referring to the possible use of a laser beam which, owing to the age of the document, is presumed to be produced by a ruby laser, U.S. Patent No. 3,657,085 does so in conjunction with the marking of mass coloured materials, i.e.

materials having a chromophore throughout their bulk and not simply ones provided with a coloured surface layer. The laser beam penetrates the spectacle lens whereupon the laser radiation is progressively absorbed by the chromophore and, in so doing, generates sufficient localised heating to produce permanent stress patterns within the material. Since the method relies upon the laser radiation being absorbed by the chromophore, in order for the resulting mark to be spaced from the surface of the material, the material must be at least partially transparent to the laser radiation used in order to allow the laser radiation to penetrate the material to the required depth.

In contrast to the method described in U.S.

Patent No. 3,657,085, the Applicant developed a different method and apparatus specifically for providing a body of glass with a sub-surface mark which are described in International Patent Publication No. WO 95/05286. The Applicant made the surprising, if not startling, discovery that a body of glass could be provided with a sub-surface mark using a CO<sub>2</sub> laser even though it was well known that glass is opaque to electromagnetic radiation having a wavelength of 10.6  $\mu$ m (the wavelength of the radiation produced by a CO<sub>2</sub> laser) and which as a result is absorbed by the glass in a thin surface layer having a depth very much less than the distance at which the desired mark is to be spaced from the surface. At the time the marking process was thought to be caused by the heating effect produced by the beam which it was supposed could be experienced outside a beam interaction volume (ie that volume of material within which an arbitrary large proportion, say 95%, of the incident beam energy is absorbed) since glass was known to have a significant coefficient of thermal conductivity.

Accordingly, it was thought that a conductive heating zone (CHZ) surrounded the beam interaction volume (BIV) and that beyond the conductive heating zone lay a stressed zone in which stresses were present which resulted from thermally induced changes in the physical dimensions of the material in the BIV and in all or part of the CHZ. It was this mechanism that was thought to explain how it was possible, using a CO<sub>2</sub> laser having a power density of between 6kW/cm<sup>2</sup> and 10kW/cm<sup>2</sup>, to create a mark within a body of glass at a depth of between 40m and 50m beyond that to which the laser radiation could penetrate.

Clearly the method and apparatus described in WO 95/05286 were highly material dependent.

Although not fully understood at the time, the material to be marked, glass, was required to absorb sufficient electromagnetic radiation of a particular wavelength to generate a thermal gradient within the material but not so large an amount as to melt the material which would have an annealing effect, relieving the stress necessary to form the mark, and which, if it occurred at the surface, would give rise to an obvious witness mark thereby destroying the covert nature of the mark. The material also had to have a thermal conductivity sufficient to enable heat generated within the beam interaction volume to be conducted away from the surface of the body to the depth at which the desired mark was to be made but not so great a conductivity as to entirely remove the thermal gradient initiated by the absorption of the laser radiation. Finally, the material to be marked also had to possess the necessary mechanical properties to inhibit the establishment of witness marks by surface cracking or otherwise which might render the resulting mark both visible to the naked eye and prone to detection by surface analysis.

By-virtue of a greater understanding of the mechanisms involved in the marking process the Applicant has been able to identify a further group of materials, other than glass, having the necessary properties and to which the method may be applied.

Accordingly, the present invention provides a method of providing a glassy thermoplastic polymeric material with a sub-surface mark, the glassy thermoplastic polymeric material having a glass transition temperature in excess of 800C and the method comprising the steps of directing at a surface of the glassy thermoplastic polymeric material a beam of laser radiation to which the glassy thermoplastic polymeric material is substantially opaque as herein defined, the beam energy absorbed at the surface of the glassy thermoplastic polymeric material being sufficient to produce localised stresses within the glassy thermoplastic polymeric material at a location spaced from said surface without any detectable change at said surface, the localised stresses thus produced being normally invisible to the naked eye but capable of being rendered visible under polarised light.

A number of embodiments of the present invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram of an apparatus capable of performing the method to be described;

Figure 2 is a schematic diagram of the way in which electrical power is distributed throughout the apparatus of Figure 1;

Figure 3 is a schematic diagram illustrating the way in which a beam of laser radiation interacts with a body of polycarbonate material;

Figure 4 is a schematic diagram of a laser power density profile capable of producing a series of marks in a dot-matrix format; and

Figure 5 is a schematic diagram of an apparatus for use in viewing the marks produced by a method in accordance with the present invention.

An apparatus capable of performing the method of marking of the present invention is shown in Figure 1. As can be seen, this apparatus comprises a source 10 which produces a beam of laser radiation 12 which is directed so as to impinge upon a body of glassy thermoplastic polymeric material such as polycarbonate 14.

In what follows it will be understood that polycarbonate is just one example of a sub-group of thermoplastic polymeric materials which it has been discovered are capable of being provided with a sub-surface mark in accordance with the present invention. This sub-group, which is here referred to as "glassy thermoplastic polymeric materials", is intended to include those thermoplastic polymeric materials which are normally in an amorphous state at 200C and which have a glass transition temperature in excess of 800C, and more preferably greater than or equal to 1000, or even 1200. Such materials include among others Acrylonitrile-Butadiene-Styrene (ABS), Acrylics such as Polymethylmethacrylate (PMMA), Cellulose Acetate, Cellulose Acetate Butyrate, Polycarbonate, Polystyrene, Polysulphone and Polyvinyl Chloride (PVC). It has been found that this sub-group of glassy thermoplastic polymeric materials display the necessary optical, thermal and mechanical properties necessary to support the marking process of the present invention.

However, of these various materials, Polycarbonate, which has the chemical formula  $(COOC_6H_5C(CH_3)_2C_6H_5O)$  and which is a synthetic thermoplastic capable of being derived from bisphenol A and phosgene, a linear polyester of carbonic acid, is particularly advantageous.

It will be appreciated that the glassy thermoplastic polymeric material may contain additives conventional in the art, such as fillers, reinforcements, plasticizers, stabilizers, flame retardants, lubricants and pigments and dyes.

Referring again to Figure 1, the source 10 is selected in such a way that the polycarbonate material is substantially opaque to the beam of laser radiation 12 produced by the source. In the particular embodiment illustrated in Figure 1, the source 10 comprises an RF excited simulated continuous-wave carbon dioxide (CO<sub>2</sub>) laser that emits a beam of laser radiation 12 having a wavelength of 10.6µm and which is consequently invisible to the naked eye. Having been emitted from the CO<sub>2</sub> laser, the beam of laser radiation 12 is incident upon a first reflecting surface 16 that directs the beam 12 through a beam expander 18 and a beam combiner 20 to a second reflecting surface 22. A second source of laser radiation, in the form of a low power He-Ne (Helium-Neon) laser 24, is disposed adjacent to the CO<sub>2</sub> laser 10 and emits a secondary beam of visible laser radiation 26 with a wavelength of 632.9nm. The secondary beam 26 impinges upon the beam combiner 20 where it is reflected towards the second reflecting surface 22 coincident with the beam of laser radiation 12 from the CO<sub>2</sub> laser 10. Thus the necessary properties of the beam combiner 20 are that it should transmit electromagnetic radiation with a wavelength of 10.6µm whilst reflecting electromagnetic radiation with a wavelength of 632.9nm. In this way the He-Ne laser beam 26 provides the combined CO<sub>2</sub>/He-Ne beam 12,26 with a visible component that facilitates optical alignment.

Once combined, the two coincident beams 12,26 are reflected at the second reflecting surface 22 to a third reflecting surface 28, and from the third reflecting surface 28 are further reflected towards a fourth reflecting surface 30. From the fourth reflecting surface 30 the combined beam 12,26 is reflected yet again toward a head unit 32 from whence the combined beam 12,26 is finally directed towards the polycarbonate material 4. In order to facilitate marking at different heights from the base of the polycarbonate material 14, the third and fourth reflecting surfaces 28 and 30 are integrally mounted, together with the head unit 32, so as to be adjustable in a vertical plane under the action of a stepping motor 34 (not shown).

Within the head unit 32 the combined CO<sub>2</sub>/He-Ne beam 12,26 is sequentially incident upon two movable mirrors 36 and 38. The first of the two mirrors 36 is disposed so as to be inclined to the combined beam 12,26 that is incident upon it as a result of reflection from the fourth reflecting surface 30 and is movable in such a way as to cause the beam reflected therefrom to move in vertical plane. The second of the two mirrors 38 is similarly inclined, this time to the beam 12,26 that is incident upon it as a result of reflection from the first mirror 36, and is movable in such a way as to cause a reflected beam 12,26 to move in a horizontal plane. Consequently, it will be apparent to those skilled in the art that the beam 12,26 emerging from the head unit 32 may be moved in any desired direction by the simultaneous movement of the first and second mirrors 36 and 38. In order to facilitate this movement the two movable mirrors 36 and 38 are mounted on respective first and second galvanometers 40 and 42. Whilst it is recognised that any suitable means may be provided to control the movement of the two mirrors 36 and 38, the approach adopted combines a speed of response with an ease of control that represents a significant advantage over alternative control means.

Emerging from the head unit 32, the combined beam 12,26 is concentrated by passing through a lens assembly 44 which may include one or more lens elements. A first lens element 46 brings the beam 12,26 to a focus at a chosen location on the surface of the polycarbonate material 14. As is well known, the maximum power density of the beam 12,26 is inversely proportional to the square of the radius of the beam 12,26 at its focus which in turn is inversely proportional to the radius of the beam 12,26 that is incident upon the focusing lens 46. Thus for a beam 12,26 of electromagnetic radiation carrying a wavelength  $\lambda$  and a radius  $R$  incident upon a lens of focal length  $f$ , the power density at the focus  $E$ , is to a first approximation, given by the expression:

$$E = \frac{P}{\pi R^2}$$
 where  $P$  is the power produced by the laser. From this expression the value and purpose of the beam expander 18 is readily apparent since increasing the radius of the beam  $R$  serves to increase the power density  $E$  at the focus. In addition, the lens element 46 is typically a short focal length lens having a focal length in the range between 70mm and 80mm so that power densities in excess of 6kW/cm<sup>2</sup> may be readily achieved at the focus of the beam 12,26.

A second lens element 48 may be placed in series with the focusing lens element 46 in order to compensate for any curvature of the surface of the polycarbonate material 14. It will be recognised that such a correcting lens will not be required if the body to be marked 14 presents a substantially planar surface to the incident beam and the need for such an element may be negated altogether if the first element 46 is of variable focal length and comprises, for example, a flat field lens. However, it is to be noted that the use of one or more optical elements is a particularly simple and elegant way of ensuring that the beam 12,26 is focused on the surface of the body 14 irrespective of any curvature thereof.

In the interests of safety, the two lasers 10 and 24 and their respective beams 12 and 26 are enclosed within a safety chamber 52 as shown in

Figure 2, with the combined beam 12,26 emerging from the safety chamber 52 only after passing through the lens assembly 44. Access to the two lasers 10 and 24 and the various optical elements disposed in the path of the respective beams 12,26 is gained by means of a door panel 54 which is fitted with an interlock 56 which prevents the operation of the CO<sub>2</sub> laser 10 and the He-Ne laser 24 while the door panel 54 is open.

A single phase electrical mains supply of 240V is fed via the door panel interlock 56 to a mains distribution unit 58 that is disposed below, and isolated from, the safety chamber 52 in order to prevent any electrical effects from interfering with the operation of the lasers 10 and 24. From the distribution unit 58, mains electrical power

is provided to the CO<sub>2</sub> laser 10 and the He-Ne laser 24 as well as to a chiller unit 60 that serves to cool the CO<sub>2</sub> laser 10. In addition mains electrical power is also supplied to the stepping motor 34 and to a computer 62.

Three AC/DC convertors and associated voltage regulators provide regulated DC voltage supplies of 12V + IOV and + 28V that are fed respectively to the He-Ne laser 24 to facilitate the pumping mechanism and to the head unit 32 where in particular, the + 28V supply is used to power the first and second galvanometers 40 and 42 and the + IOV supply fed to the galvanometers to produce a predetermined movement of the first and second mirrors 36 and 38. Thus by using the computer 62 to modulate the + IOV supply the various movements of the first and second galvanometer mirrors 36 and 38 may be made under the control of a computer programme.

In use, the beam of laser radiation 12 emitted by the CO<sub>2</sub> laser 10 is caused to form an illuminated spot at a location on the surface of the polycarbonate material 14, the body to be marked. This spot may then be scanned across the surface of the body as a result of the movement of one or both of the galvanometer mirrors 36 and 38.

Glassy polymeric materials and in particular polycarbonate materials such as LEXAN PKG1643, LEXAN PK2870 and LEXAN 164R, all available from General Electric Plastics B.V. of Plasticlaan 1, P O Box 117, NL-46000, AC Bergen Op Zoom, The Netherlands, are opaque to electromagnetic radiation having a wavelength of 10.6cm. Despite this the Applicant has established that it is possible to provide these materials with a sub-surface mark using a CO<sub>2</sub> laser.

As with the marking of glass described in WO 95/05286, it is important to remember that the absorption of a beam of laser radiation by a material is a progressive or statistical process and that the beam energy is always absorbed in a

Beam Interaction Volume (BIV) of finite dimensions. Thus in this context a Beam Interaction Volume may be defined as that volume within which an arbitrarily large proportion, say 95%, of the incident beam energy is absorbed. For electromagnetic radiation within the visible region of the electromagnetic spectrum and glassy thermoplastic polymeric materials which are transparent at those wavelengths, the BIV may be very large compared to the dimensions of the body concerned. By contrast, for electromagnetic radiation having a wavelength of 10.6cm, experiments have shown the same glassy thermoplastic polymeric materials to have a BIV having a depth in the direction of propagation of the beam of between 8.0m and 16.0m for a beam having a power density within the range from 6 to 10 kW/cm<sup>2</sup>. Thus, whilst for most practical purposes the beam of laser radiation 12 may be thought of as being absorbed "at the surface" of the polycarbonate material 14, the fact that a dimension of even 8.0m is readily observed using electron microscopical techniques means that it is necessary to further define what is to be understood by the term opaque. Thus, for the avoidance of doubt, in the present context the term opaque, when used to describe the material to be marked, refers to a material capable of absorbing 95% of the energy of an incident beam of laser radiation within a distance which is less than that at which the sub-surface mark is spaced from the surface.

Despite 95% of the energy of the laser radiation being absorbed within the BIV, the effect of the beam on the polycarbonate material is not confined to this surface region. For example, the heating effect produced by the beam may be felt at a location outside the BIV since polycarbonate and other glassy thermoplastic polymeric materials have a significant coefficient of thermal conductivity of between 0.10 and 0.22 W/mOC. For example, LEXAN PKG1643 and LEXAN 164R both have a thermal conductivity of 0.20 W/mOC while LEXAN PK2870 has a thermal conductivity of 0.19 W/mOC. Likewise, any resulting stress pattern may also extend beyond the region of the polycarbonate material that is directly affected by the laser beam in just the same way that the stress pattern in a pane of glass extends beyond the tip of a crack that is propagated therein.

Thus it will be appreciated that in principle, the physical consequences of irradiation can be observed at a location remote from the BIV.

This situation is summarised in Figure 3 in which there is illustrated a body of glassy thermoplastic polymeric material having a BIV in which an arbitrary proportion of an incident beam energy is lost to the material.

Surrounding the BIV is a Conductive Heating Zone (CHZ) whose boundary, like that of the BIV, must again be defined in terms of arbitrary limits. Beyond the Conductive Heating Zone lies a stressed zone in which the stresses result from thermally-induced changes in the physical dimensions of the material in the BIV and in all or part of the CHZ. The variation in magnitude of these stresses as a function of the radial distance from the incident beam is indicated by means of the curve 66 from which it can be seen that a line of peak stress 68 may be drawn a short distance from the boundary of both the BIV and the CHZ.

It has been found that using a CO<sub>2</sub> laser having a power density of between 6kW/cm<sup>2</sup> and 10kW/cm<sup>2</sup> it is possible to create a mark within a body of polycarbonate material at a depth of between 40m and 50m beyond that to which the laser radiation penetrates. This mark, which in cross-section has the shape of a convex lens element, typically has a depth (i.e. a dimension in the direction of the beam) of 10.8m and a diameter of 125m and is thought to be caused as a result of a thermal interaction within the polycarbonate material.

In this context it is to be noted that the possible types of interaction between laser radiation and a body of material may be categorised under three headings dependant upon the power density of the laser radiation concerned. In order of increasing power density these headings are as follows:

1. Photochemical interactions including photoinduction and photoactivation.
  2. Thermal interactions in which the incident radiation is absorbed as heat; and
  3. Ionising interactions which involve the non-thermal photodecomposition of the irradiated material.
- The difference between the thresholds of these three interactions is clearly demonstrated by comparing the typical power density of 10-3 W/cm2 required to produce a photochemical interaction with the power density of 1012 W/cm2 typical of ionising interactions such as photoablation and photodisruption.

The lens-shaped mark, which is invisible to the naked eye but which, assuming the glassy thermoplastic polymeric material to be transparent to electromagnetic radiation within the visible region of the electromagnetic spectrum, can be viewed using a compound microscope under both bright field illumination and when viewed between crossed polarizing filters, has been observed to have a sharply-defined lower edge. This observation has led to the speculation that the mark represents the boundary between those molecules within the glassy thermoplastic polymeric material that derive sufficient energy from the incident beam to overcome the bonds with which they are tied to their neighbours and those that do not. As might be expected from this model, a stressed region extends beyond the lower edge of the lens-shaped mark and into the body of the material. This stressed region, which may have a dimension in the direction of the beam of up to 60cm, is also invisible to the naked eye but may be rendered visible under polarized light.

It has been found that the lens-shaped mark and the associated stressed region may only be created using a CO2 laser beam having an energy density falling within a narrowly defined range. If the energy absorbed by the glassy thermoplastic polymeric material is too small then an insufficient thermal gradient is established to give rise to an observable stressed region.

Conversely, if too high an energy is absorbed, the surface of the glassy thermoplastic polymeric material may melt or else the polycarbonate material may crack along a line of peak stress and flake off. This cracking of the material, known as "breakout", not only relieves the stress in what remains of the glassy thermoplastic polymeric material but also renders the mark both visible to the naked eye and prone to detection by surface analysis. However, it is a characteristic of glassy thermoplastic polymeric materials as herein defined that they have impact properties which can be categorised as being either "notch brittle" or "tough", meaning that test specimens do not break if un-notched. Preferably the material to be marked has a hardness value measured on the Rockwell scale of between R70 and R125.

In the embodiment described, the beam of laser radiation 12 is scanned across the surface of the polycarbonate material 14 at an average speed of 2 to 3m/s to produce patterns which may be used to relate to alpha-numeric characters.

However, rather than moving at a constant speed from one end of a straight line scan to the other, the beam is scanned in a series of incremental steps which serve to increase the definition and resolution of the characters thus produced. As a result, the velocity of the beam varies in a manner which is approximately sinusoidal between zero when the beam is at either end of one of its incremental steps, and so is effectively at rest, and approximately 3m/s at a point midway between these two ends. Consequently, even though the power density of the beam is kept constant, different points on the surface of the polycarbonate material are exposed to different beam energies. It has been found that the energy density window for the generation of the aforementioned mark is sufficiently narrow that the lens-shaped mark and its associated stressed region are only observed at those points at which the beam is effectively at rest. The result of this is that under polarized light, the stressed regions created by scanning the laser beam across the surface of the bottle show up as a series of dots. Thus by controlling the movement of the galvanometer-mirrors 36 and 38 it is possible to scan the laser beam 12 across the surface of the polycarbonate material 14 in such a way as to "write" any desired symbol on to the material in a dot matrix format.

In an alternative embodiment the same dot matrix format may be achieved by scanning the beam across the surface of the glassy thermoplastic polymeric material at a constant speed whilst periodically varying its power density between two levels either side of the threshold for creating the lens-shaped mark and its associated stress pattern. This type of varying power density might, for example, be achieved by superimposing a sinusoidal ripple 70 on top of a square wave pulse of laser radiation 72 as shown schematically in Figure 4. Assuming that the threshold for creating the aforementioned mark is at a power level represented by the dashed line 74 one might expect to see dot-like regions of stress within the glassy thermoplastic polymeric material spaced apart by a distance corresponding to that scanned by the laser beam between successive maxima 76 of the power density profile 78.

In both of the foregoing embodiments it is thought that the gradual increase in energy absorbed by the glassy thermoplastic polymeric material at points closer to that at which a mark is actually created provides the material with a limited ability to anneal itself. This is to be contrasted with an arrangement in which the laser beam is pulsed to generate a series of marks at locations spaced an arbitrary distance apart. The self-annealing nature of the aforementioned embodiments is considered to provide a marked body whose strength is not compromised by the marking process.

The patterns of consecutive dots created by the methods described also result in a local reversal in the orientation of the stressed regions within the polycarbonate material and thus in the plane of polarization of any light caused to pass through them. This facilitates the detection of the marks and gives rise to a characteristic "cross-stitch" pattern.

In a further embodiment, rather than creating a pattern of dots, the described apparatus may be used to create a mark comprising one or more continuous lines. To this end the beam of laser radiation 12 may be scanned across the surface of the body to be marked at a constant velocity while at the same time the power density of the beam is maintained at a constant level just above the threshold for creating the lens-shaped mark and its associated stress pattern.

In yet another embodiment, rather than scanning the beam of laser radiation 12 across the surface of the polycarbonate material 14, the beam may be used to illuminate a mask. By placing the mask in front of the polycarbonate material and providing the mask with one or more apertures, selected portions of the incident beam may be caused to impinge upon the material and so produce a mark of a predetermined shape.

In order to observe the marks produced in accordance with any of the foregoing embodiments in bodies formed of glassy thermoplastic polymeric materials which are transparent to electromagnetic radiation within the visible region of the electromagnetic spectrum, the marked body may be placed between a pair of crossed linear polarizers and illuminated with a powerful collimated light beam. As a result the stressed regions are rendered visible as bright areas against a dark background. An example of such an apparatus is shown in Figure 5 to comprise a housing 100 similar to that used as the base of an overhead projector in which there is disposed a lamp 102.

The housing 100 is provided with an upper working surface of glass 104 and between this surface and the lamp 102 there is provided a Fresnel lens 106 capable of providing basic beam collimation. The crossed linear polarizing filters 108 are inserted between the working surface 104 and the Fresnel lens 106 while in order to maintain the apparatus at a safe working temperature, the housing 100 is provided with a fan 110 of the type used in computer systems as well as a louvred opening 112 for the passage of air. A dimmer switch may be provided to control the intensity of the lamp 102.

In order to observe the stressed regions within the glassy thermoplastic polymeric material 14, the body is placed on top of the working surface 104 and viewed using a x10 magnifier 114 fitted with a suitable filter 116.

In cases where the glassy thermoplastic polymeric material is opaque to electromagnetic radiation within the visible region of the electromagnetic spectrum, the localised stresses may still be detected using optical instruments operating at an appropriate wavelength within the electromagnetic spectrum to which the material concerned is transparent.

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## Claims

### CLAIMS:

1. A method of providing a glassy thermoplastic polymeric material with a sub-surface mark, the glassy thermoplastic polymeric material having a glass transition temperature in excess of 800C and the method comprising the steps of directing at a surface of the glassy thermoplastic polymeric material a beam of laser radiation to which the glassy thermoplastic polymeric material is substantially opaque as herein defined, the beam energy absorbed at the surface of the glassy thermoplastic polymeric material being sufficient to produce localised stresses within the glassy thermoplastic polymeric material at a location spaced from said surface without any detectable change at said surface, the localised stresses thus produced being normally invisible to the naked eye but capable of being rendered visible under polarised light.
2. A method in accordance with claim 1, wherein the glassy thermoplastic polymeric material has a glass transition temperature greater than or equal to 1000C.
3. A method in accordance with claim 1 or claim 2, wherein the glassy thermoplastic polymeric material has a glass transition temperature greater than or equal to 1200C.
4. A method in accordance with any preceding claim, wherein the glassy thermoplastic polymeric material has a glass transition temperature greater than or equal to 1400C.
5. A method in accordance with any preceding claim, wherein the glassy thermoplastic polymeric material has a thermal conductivity of between 0.10 and 0.22 W/mOC.
6. A method in accordance with any preceding claim, wherein the glassy thermoplastic polymeric material has impact properties such that the glassy thermoplastic polymeric material is classified as notch brittle or tough.
7. A method in accordance with any preceding claim, wherein the glassy thermoplastic polymeric material has a hardness value on the Rockwell scale of between R70 and R125.
8. A method in accordance with any preceding claim, wherein the glassy thermoplastic polymeric material is selected from the list comprising  
Polycarbonate, Polymethylmethacrylate (PMMA),  
Polystyrene, Polyacrylonitrile, Acrylonitrile  
Butadiene-Styrene (ABS), Polyvinyl Chloride (PVC),  
Polybutyleneterephthalate, Polyphenylene Sulphide,  
Polyetheretherketone, Acrylic, Polysulphone,  
Cellulose Acetate, and Cellulose Acetate Butyrate.
9. A method in accordance with any preceding claim, wherein the mark created by the localised stresses is representative of one or more numerals, letters or symbols or a combination thereof.
10. A method in accordance with any preceding claim, wherein the beam of laser radiation is concentrated so as to form an illuminated spot at a location on the surface of the glassy thermoplastic polymeric material, the spot being moveable relative to the glassy thermoplastic polymeric material thereby enabling the mark created by the localised stresses to be of a predetermined shape.
11. A method in accordance with claim 10, wherein the spot is moved relative to the glassy thermoplastic polymeric material in such a way as to produce an elongate region of localised stresses that when rendered visible under polarized light has the appearance of a line.
12. A method in accordance with claim 10, wherein the spot is moved relative to the glassy thermoplastic polymeric material in such a way as to produce a series of spaced apart regions of localised stresses that when rendered visible under polarized light has the appearance of a series of dots.
13. A method in accordance with claim 12, wherein the series of spaced apart regions of localised stresses are formed by moving the spot at a constant speed relative to the glassy thermoplastic polymeric material and periodically varying the power density of the beam.
14. A method in accordance with claim 12, wherein the series of spaced apart regions of localised stresses are formed by maintaining the power density of the beam substantially constant and varying the time the spot is used to illuminate successive locations on the surface.
15. A method in accordance with claim 14, wherein the spot is moved relative to the glassy thermoplastic polymeric material at a speed that varies periodically between zero and 3m/s.
16. A method in accordance with claim 15, wherein the spot is moved relative to the glassy thermoplastic polymeric material at an average speed in the range from 2 to 3m/s.



17. A method in accordance with any of claims 12 to 16, wherein the beam energy absorbed at successive locations on the surface varies smoothly from one location to the next.
18. A method in accordance with any of claims 10 to 17, wherein the laser radiation has a power density at the spot of up to 10kW/cm<sup>2</sup>.
19. A method in accordance with any of claims 1 to 9, wherein the beam of laser radiation is caused to illuminate a mask placed in front of the glassy thermoplastic polymeric material, the mask having one or more apertures thereby enabling the mark created by the localised stresses to be of a predetermined shape.
20. A method in accordance with any preceding claim, wherein the beam of laser radiation is generated by a CO<sub>2</sub> laser.
21. A method in accordance with any preceding claim, wherein the glassy thermoplastic polymeric material is transparent to electromagnetic radiation at wavelengths within the visible region.
22. A method in accordance with any claims 1 to 20, wherein the glassy thermoplastic polymeric material is opaque to electromagnetic radiation at wavelengths within the visible region such that the localised stresses may only be seen by optical instruments operating at an appropriate wavelength within the electromagnetic spectrum.
23. A method of providing a glassy thermoplastic polymeric material with a sub-surface mark substantially as herein described with reference to the accompanying drawings.
24. A body of glassy thermoplastic polymeric material comprising a mark obtainable in accordance with any of the methods of claims 1 to 23.
25. A body of glassy thermoplastic polymeric material in accordance with claim 24 wherein the mark created by the localised stresses is representative of one or more numerals, letters or symbols or a combination thereof.
26. A body of glassy thermoplastic polymeric material substantially as herein described with reference to the accompanying drawings.

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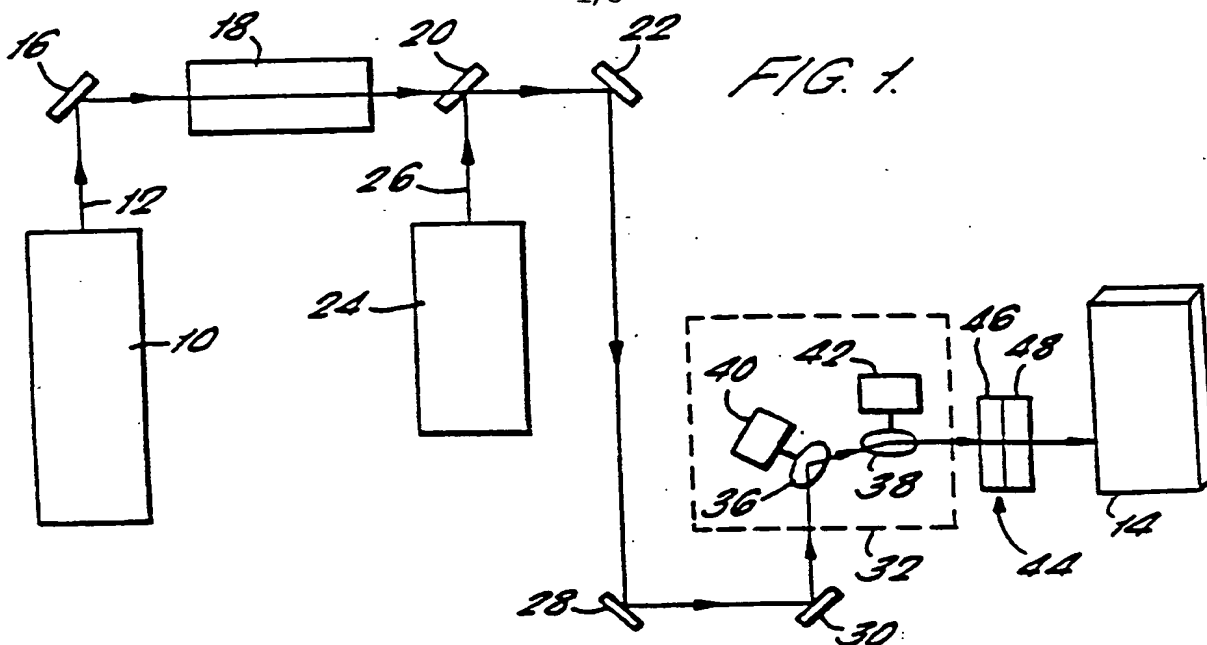
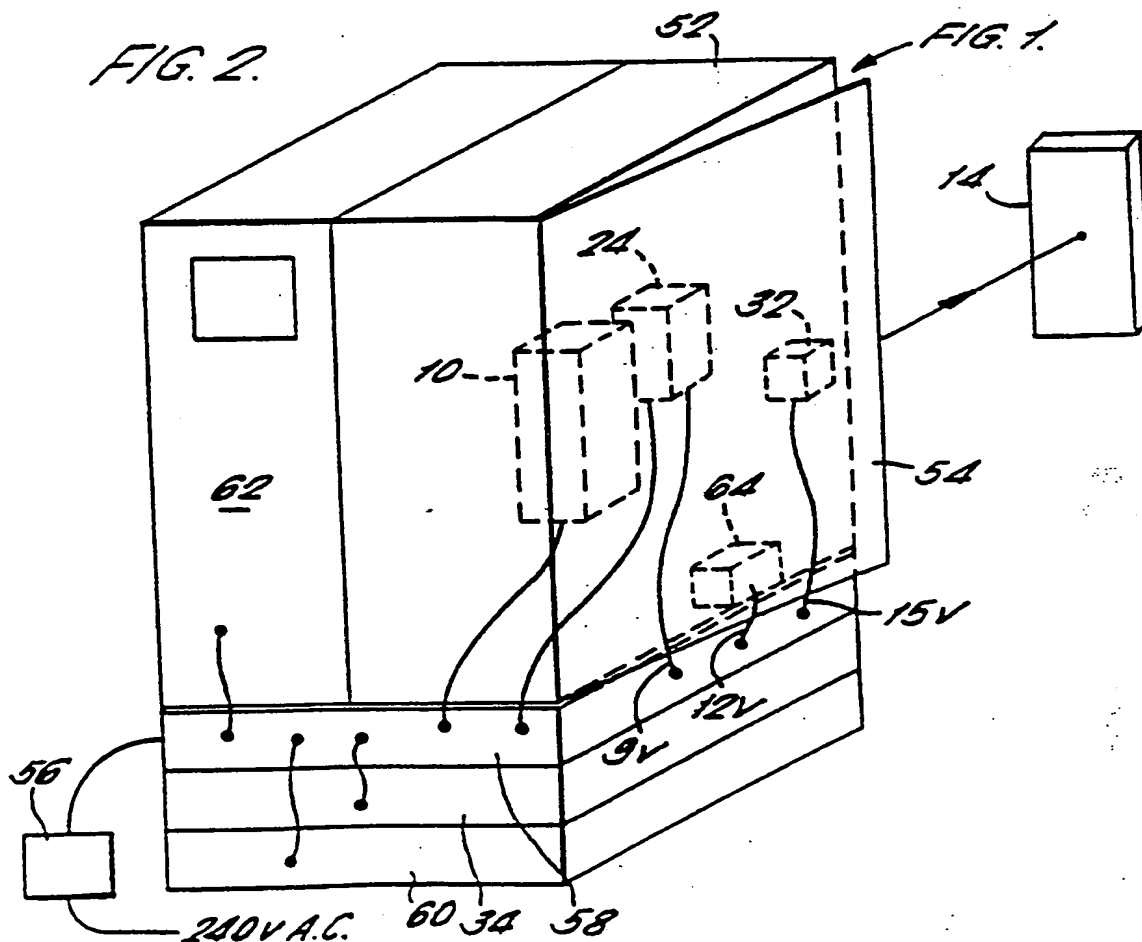


FIG. 2.



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FIG. 3.

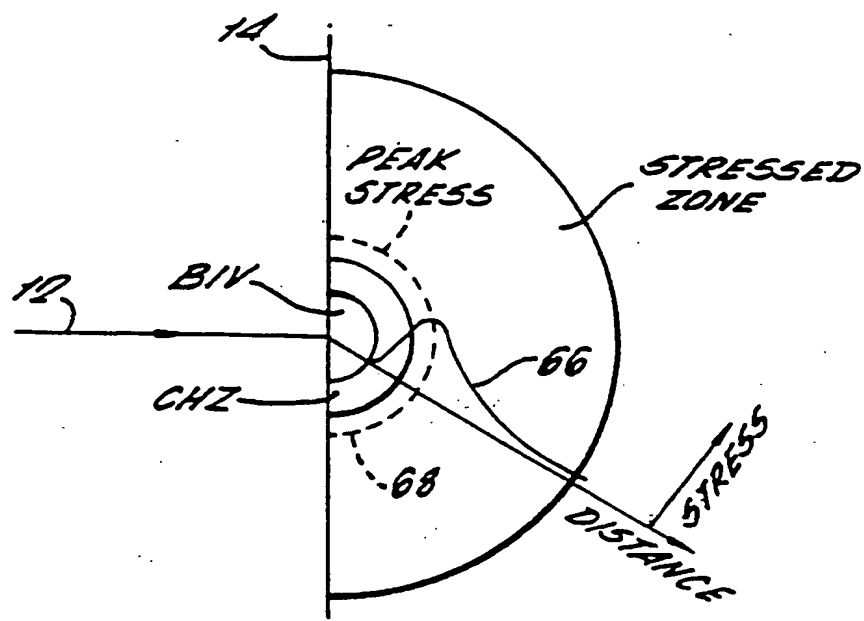
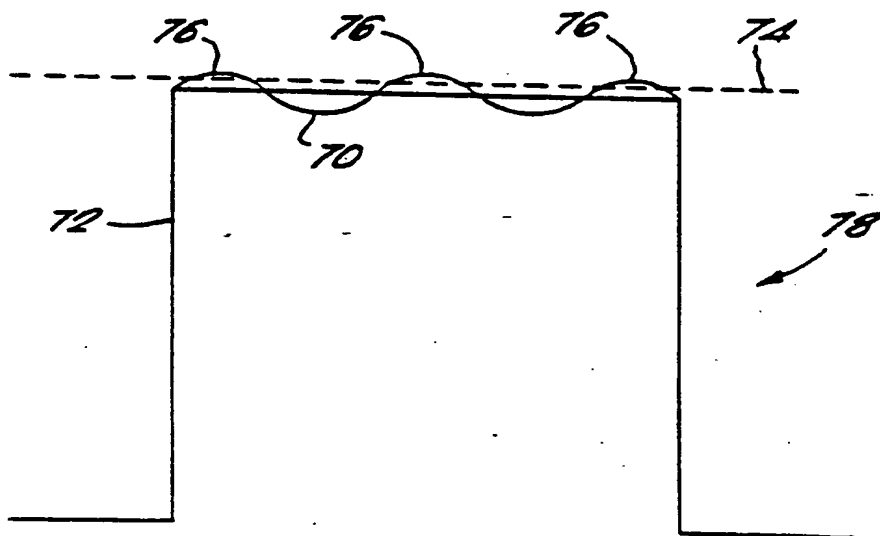


FIG. 4.



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FIG. 5.

